

L109,473



PATENT SPECIFICATION

NO DRAWINGS

L109,473

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COMPLETE SPECIFICATION

Improvements in or relating to Diazotype Materials

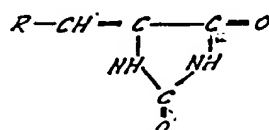
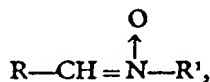
We, GENERAL ANILINE & FILM CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America of 140 West 51st Street, New York, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to light-sensitive diazotype materials containing ultraviolet absorbing compounds and particularly the utilization of such compounds, the ultraviolet absorbing properties of which are destroyed by exposure to actinic light.

The incorporation of ultraviolet light absorbers in diazotype materials has been adopted for the purpose of copying continuous tone originals. However, while the incorporation of the ultraviolet absorbers permits the attainment of this result, the residual ultraviolet absorber which remains in the print slows down the reprint speed. In addition, the retained ultraviolet absorber causes background yellowing of the print.

We have found that improved results may be achieved by incorporating into diazotype materials U.V. absorbers which are effective in screening out radiation in the 340 to 390 mμ range but which upon being struck by radiation to which the diazonium compound is sensitive are modified so that they are no longer capable of absorbing light in the above range.

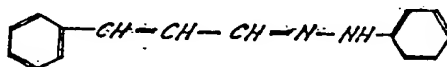
Compounds meeting these prerequisites are those represented by the following general formulae:

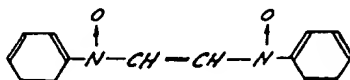


wherein R or R¹ is aryl, e.g. phenyl, naphthyl, or substituted aryl such as acyloxyphenyl, e.g. acetoxyphenyl, benzoyloxyphenyl; alkoxyphenyl, e.g. methoxyphenyl, ethoxyphenyl, propoxyphenyl; halophenyl; e.g. chlorophenyl, bromophenyl; or aralken such as styryl, or a heterocyclic radical such as thienyl or furfuryl; and n is 1 or 2.

Examples of compounds within the above classification are:

(1) Cinnamaldehyde phenylhydrazone

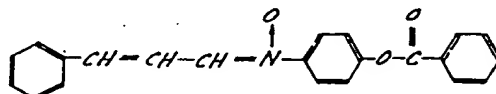


(2) *N,N'*-Diphenyl- α , α' -dinitrone

Prepared according to the method of v. Pechmann, Ber. 30, 2462, 1897.

(3) *N*-*p*-Benzoylphenyl- α -styrylnitron

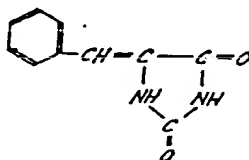
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Prepared according to the methods described in Ber. 36, 415 (1903).

(4) 5-Benzylidenehydantoin

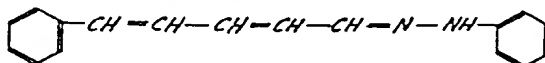


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Prepared according to the method disclosed in J. Am. Chem. Soc. 37, 385 (1915).

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(5) 5-Phenyl-1-penta-2,4-dienal phenylhydrazone

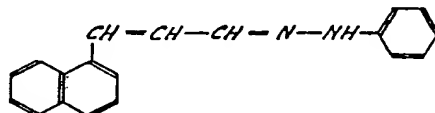


Prepared according to Ber. 58B, 1284—90 (1925) by the condensation of phenylhydrazine and 5-phenyl-1-pentadienal, m.p. 170—2°C.

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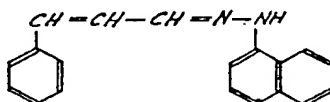
(6) 1-Naphthaleneacrolein phenylhydrazone

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Prepared according to Chem. Ber. 91, 1867—81 (1958), m.p. 125—6°C.

(7) Cinnamaldehyde-1-naphthylhydrazone

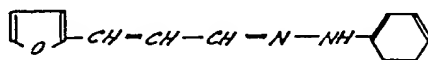


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Prepared according to Atti reale accd.naz.Lincei (5) 18 II (1909), 270 m.p. 165°C.

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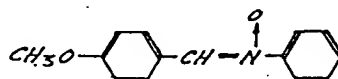
(8) 2-Furanacrolein phenylhydrazone



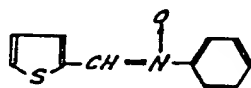
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Prepared according to Bull. Soc. Chim. France 35, 1685—65 (1924)

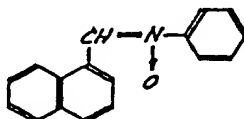
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(9) α (*p*-Methoxyphenyl)*N*-phenylnitronPrepared according to Ann. 367, 272 (1909) by the condensation of anisaldehyde and *N*-phenylhydroxylamine in ethanol, m.p. 116.5—117.5°C.

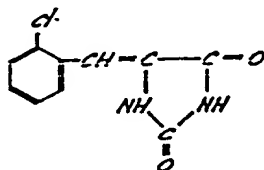
(10) N-Phenyl-alpha-2-thienylnitron



Prepared by the condensation of 2-thiophenealdehyde and N-phenylhydroxylamine in ethanol, m.p. 89—90.5°C.

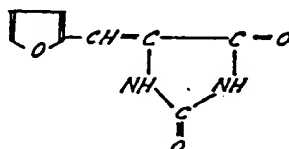
(11) *alpha*-1-Naphthyl-N-phenylnitron

Prepared by the condensation of 1-naphthaldehyde and N-phenylhydroxylamine in ethanol, m.p. 133—135°C.

(12) 5-(*o*-Chlorobenzylidene)hydantoin

Prepared according to J. Am. Chem. Soc. 62, 567 (1940) by the condensation of *o*-chlorobenzaldehyde and hydantoin in glacial acetic acid, acetic anhydride and fused sodium acetate; m.p. 275°C.

(13) 5-Furfurylidenehydantoin



Prepared according to J. Am. Chem. Soc. 45, 380-(1911), m.p. 232°C.

TABLE I

Compound Name (Solvent)	Wavelength of Max. Absorption μ	Molar Absorptivity
(1) Cinnamaldehyde phenylhydrazone (ethanol)	360	3.93×10^4
(2) N,N'-Diphenyl-alpha, alpha-dinitron (ethanol)	385	2.57×10^4
(3) N-p-Benzoxyphenyl- alpha-stearyl-nitron (chloroform)	360	2.74×10^4
(4) 5-Benzylidenehydantoin (ethanol)	315	2.25×10^4

The ultraviolet light absorbers may be incorporated in the sensitizing solution or in a wide variety of organic carrier base materials, particularly, compositions which are water-white or substantially colourless, including film-forming plastics or resins.

The ultraviolet light absorbers may be incorporated into solutions or dopes of the said film-forming materials by forming a solution of the ultraviolet light absorbers in a suitable solvent mutually compatible with the dope, casting coating or otherwise treating this solution to form a sheet or foil and, finally, driving off the solvent.

The amount of ultraviolet light absorbers to be employed in the foregoing coatings is not critical, and the actual concentration to be employed may be very readily determined by a simple trial experiment. It will be appreciated that each type of material may require an amount which will differ from a closely analogous material. For practical purposes, it has been found that the amount may range from 0.1 percent to 5 percent based on the dry weight of the coating material.

Any of the usual light-sensitive diazonium compounds may be employed and, in this connection, reference is made to the compounds referred to in U.S. Patent Specification 2,501,874, and in the article by van der Grinten, *Photographic Journal*, Vol. 92B, 1952, page 46. The stabilized diazonium salts from N,N-disubstituted p-phenylenediamines are most satisfactory. Examples of such diazonium salts are those derived from N,N-diethyl-p-phenylenediamine; N-benzyl-N-ethyl-6-phenylenediamine; N-ethyl-p-phenylenediamine; N-phenyl-p-phenylenediamine; N,N-diethyl-2-ethoxy-p-phenylenediamine; N-ethyl-2-methyl-p-phenylenediamine; N,N-bis (2-hydroxyethyl)-p-phenylenediamine; and N-2-hydroxyethyl-N-methyl-p-phenylenediamine. According to customary procedure, these diazonium salts are used in the form of salts stabilized with zinc chloride, tin chloride and cadmium chloride.

The comments with regard to the diazonium compounds apply equally to the coupling components. Thus, any of the usual coupling components are satisfactory for our purposes. Examples of such couplers are 2,5-xyleneol; 2,3-dihydroxynaphthalene; 1,8-dihydroxynaphthalene; resorcinol; octyl resorcinol; 3-methyl-4-phenyl-5-pyrazolone; the amide of *alpha*-resorcylic acid; H acid; acetoacetanilide and 6,7-dihydroxynaphthalene-1-sulphonic acid. Other couplers are mentioned in the van der Grinten article *supra*.

The coating solution, in addition to the ultraviolet light absorbers and light-sensitive diazo may contain the various adjuncts usual in the manufacture of light-sensitive diazotype materials. These include metal salts for intensification of the dye-stuff image, such as ammonium sulphate, nickel sulphate and zinc chloride; stabilizing agents such as thiourea, thiosinamine and naphthalenetrisulphonic acid; acids acting to retard precoupling such as acetic acid, boric acid and tartaric acid; hygroscopic agents such as glycol and glycerol; and wetting agents such as saponin, lauryl sulphonate, butylbenzene sulphonate and the oleic acid amide of N-methyl taurine.

In producing a diazotype light-sensitive layer from coating solutions containing the ultraviolet absorber compounds used in this invention, the base or support material may be dipped, brushed or sprayed with the sensitizing or coating solution by means known to the art, the particular type of application depending upon the carrier employed. Where paper is used as the base for the light-sensitive coating, the coating solution is generally applied by using a trough and doctor blade, the paper being drawn past the trough and excess solution being scraped off with the doctor blade. The paper may also be brushed or sprayed with the coating solution. When a film material is used as the support, in order to obtain proper penetration of the active agents, solvents or swelling agents may be added to the coating solution and the solution is generally applied by dipping.

The following examples will serve to further illustrate the preparation of diazotype photoprinting materials from the ultraviolet absorber compounds of this invention, it being understood that the invention is not limited to the particular materials or proportions therein described. Unless otherwise specified, the parts are by weight.

EXAMPLE I

The following solution was prepared:

Acetone	70 ml
Cellulose acetate	0.4 g
2-Methoxyethanol	30 ml
Sulphosalicylic acid	1.4 g
Zinc chloride	0.16 g
3,3'-Dihydroxy-2-naphthanilide	0.51 g



<i>m,m'</i> -Ethylenedioxydiphenol	1.6 g
4,4'-Diresorcinol	0.12 g
<i>p</i> -Diethylaminobenzenediazonium chlorozincate	0.23 g
5-Benzylidenchydantoin (U.V. absorber)	1.25 g

This solution was coated on cellulose triacetate base and the dried film was exposed to ultraviolet light emitted by a mercury arc under a transparent microfilm image. Upon development with ammonia this gave a black reproduction of the original with clear non-image areas. When used as the original in the preparation of a second generation diazotype, this print, when compared with a print obtained from a conventional continuous tone formulation containing 2,2'-dihydroxy-4,4'-dimethoxybenzophenone as the ultraviolet light absorber, could be exposed for a much shorter time to give diazotype prints of equal density.

A solution of this compound coated on a cellulose acetate base was shown by spectrophotometric methods to have decomposed 76% after two passes through a white-print machine at speed 3 (3 ft. per minute).

EXAMPLE II

The coating solution of Example I was modified by substituting 1.25 grams of *N,N'*-diphenyl- α,α' -dinitrone as the U.V. absorber. The solution was coated on cellulose acetate film and was shown by spectrophotometric methods to have decomposed 96% after one pass through a white-print machine at speed 5.

The coated film also had the desirable property of a faster reprint speed in a diazotype process.

EXAMPLE III

The coating solution of Example I was modified by the substitution of 1.25 grams of *N-p*-benzoxyphehyl- α -styryl-nitron as the U.V. absorber.

The coating solution containing the ultraviolet light absorber was coated on a cellulose acetate film and was found by spectrophotometric methods to have been 90% decomposed after one pass through a white-print machine at speed 5.

The films prepared using this compound had the expected faster reprint property.

EXAMPLE IV

The coating solution of Example I was modified by the substitution of 1.25 grams of cinnamaldehyde phenylhydrazone as the U.V. absorber.

The solution was coated on cellulose triacetate base and the dried film treated in accordance with the procedure outlined in Example I. The diazotype coating displayed the expected increase in reprint speed.

A cellulose acetate film coated with a solution containing this compound was shown by spectrophotometric methods to have been 11% decomposed after one pass through a white-print machine at speed 5.

EXAMPLE V

The procedure was the same as in Example I excepting there was used 1.25 g. cinnamaldehyde 1-naphthylhydrazone as the U.V. absorber.

The results on processing were substantially the same as in Example I.

EXAMPLE VI

The procedure was the same as in Example I excepting that the U.V. absorber employed was 1.25 g. N-phenyl-alpha-2-thienyl-nitron.

The results were about the same as in Example I.

EXAMPLE VII

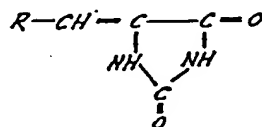
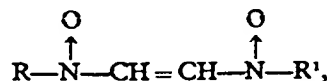
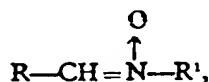
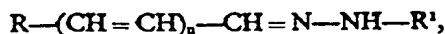
The procedure was the same as in Example I excepting that the U.V. absorber was 1.25 g. 5-(alpha-chlorobenzylidene)hydantoin.

The favorable results of Example I were obtained in this instance.

Any of the U.V. absorbers previously mentioned may be utilized in lieu of those of the Examples with equally good results.

WHAT WE CLAIM IS:—

1. A diazotype material comprising a base coated with a sensitive composition containing a light-sensitive diazonium compound and an ultraviolet absorber which is decomposed by radiation to which the diazonium compound is sensitive and which is any one of the compounds represented by the following general formulae:



wherein R, R¹ and n are as hereinbefore defined.

2. The material as defined in Claim 1, wherein the ultraviolet absorber is cinnamaldehyde phenylhydrazone.

3. The material as defined in Claim 1, wherein the ultraviolet absorber is N,N'-diphenyl-alpha, alpha'-dinitrone.

4. The material as defined in Claim 1, wherein the ultraviolet absorber is N-p-benzoxypheyl-alpha-styryl-nitron.

5. The material as defined in Claim 1, wherein the ultraviolet absorber is 5-benzylidenehydantoin.

6. The article as defined in Claim 1, wherein the sensitive composition also contains a coupling component.

7. A diazotype material according to Claim 1 substantially as herein described and exemplified.

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